

Condensation of Poly(4-vinylacetophenone) with Various Araldehydes*

C. C. UNRUH and A. C. SMITH, JR.

Research Laboratories, Eastman Kodak Company, Rochester, New York

INTRODUCTION

In an earlier publication¹ the condensation products of poly(4-vinylacetophenone) with benzaldehyde were described. Depending upon the reaction conditions used, a series of compositions was obtained which could be considered to consist of copolymers of vinylacetophenone and vinylbenzalacetophenone. The ultimate product was essentially poly(4-vinylbenzalacetophenone).

It is obvious that a number of substituted benzaldehydes or other araldehydes could be used in place of benzaldehyde. It seemed of interest to examine such condensations and to compare them with the reaction and products described earlier. Poly(4-vinylbenzalacetophenone) is not readily analyzed by conventional chemical procedures with a high degree of accuracy. In order to obtain some insight into the condensation reaction, a substituted benzaldehyde was selected whose substituent was such that it would lend itself readily to a standard chemical analysis. *p*-Methoxybenzaldehyde or anisaldehyde was selected for this purpose.

A number of substituted benzaldehydes (other than anisaldehyde) were condensed with poly(vinylacetophenone) under a standard set of conditions. Owing to adverse solubility characteristics, still other substituted benzaldehydes could not be examined under these standard conditions, and modifications were introduced in the condensation of these aldehydes.

As was indicated in the case of the condensation of poly(4-vinylacetophenone) with benzaldehyde, undesirable side reactions accompany the expected one, with the result that insoluble polymeric products would be formed. This was also generally true in the case of the substituted benzaldehyde condensation products. In fact, in nearly all instances, the pure poly(4-vinylaralacetophenone) was not attained, the reaction being stopped at an inter-

mediate stage to prevent crosslinking. The products, then, are largely copolymers of poly(4-vinylacetophenone) and varying proportions of the poly(4-vinylaralacetophenone). However, comparisons can be made between the various products which have comparable molar proportions of the aralacetophenone component.

Generally, acid catalysis was used in condensations run in media free from water. If the nature of the reactants or of the product required the presence of water to maintain solution, it was found that alkaline catalysis was preferable in those instances.

EXPERIMENTAL

The poly(4-vinylacetophenone) used in all these experiments was made as described earlier,¹ a polystyrene having an $[\eta]$ of 1.06 in chloroform (2.5 g./l.) being used.

(a) Reaction between Poly(4-vinylacetophenone) and Anisaldehyde

In this study, dioxane was used as the solvent, and the catalyst consisted of a solution of concentrated sulfuric acid in glacial acetic acid in the concentrations indicated. (Using dioxane instead of glacial acetic acid gave essentially the same results but practically it was more convenient to use the latter.) The polymer concentration in the reaction mixture was kept constant in each series, but the anisaldehyde and catalyst concentrations were varied. In the series where the amount of anisaldehyde used was varied, a correspondingly smaller or greater amount of solvent was used to maintain equivalent polymer concentrations. All reactions were carried out under very subdued light at room temperature (thermostatted at 75°F.).

The general procedure used was as follows. Seventy-three grams (0.5 mole) of poly(4-vinylacetophenone) was dissolved in the dioxane and anisaldehyde to be used. The catalyst was added, with ef-

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ficient stirring, to this solution contained in a capped, brown bottle. Aliquots of this solution were withdrawn at various intervals and a slight excess of sodium acetate (as a 10% solution in glacial acetic acid) was added in order to destroy the sulfuric acid catalyst. The solution was poured in a thin stream into a large volume (2 l.) of agitated methanol. The yellow, fibrous polymer was rapidly washed with several portions of methanol and redissolved in a mixture of dioxane and acetone, about a 5% solution of polymer being obtained. The solution was poured in a thin stream into a large volume (2 l. or more) of distilled water and the fibrous precipitate washed thoroughly in distilled water. The product was dried in the dark at room temperature.

The products were analyzed for methoxyl content by two independent analysts using Zeisel's method. Agreement was usually excellent in the

TABLE I

The Condensation of Poly(4-vinylacetophenone) with Anisaldehyde

73 g. Poly(4-vinylacetophenone) (0.5 mole); 136 g. Anisaldehyde (2 mole equivalents); 1 kg. Dioxane; 73 g. Catalyst Solution (10% by Weight of Conc. H_2SO_4 in Glacial Acetic Acid)

Expt. no.	Reaction time, hr.	Yield, g.	Anisalacetophenone, mole-%	Sensitivity value
1	24	9.4	5.4	28
2	48	9.5	7.8	160
3	72	10.0	11.4	350
4	96	10.2	14.2	650
5	144	10.4	17.5	1000
6	192	11.0	24.5	1800
7	265	11.8	29.8	2800
8	433	—	40.6	Indefinite

TABLE II

The Condensation of Poly(4-vinylacetophenone) with Anisaldehyde

73 g. Poly(4-vinylacetophenone) (0.5 mole); 136 g. Anisaldehyde (2 mole equivalents); 1 kg. Dioxane; 73 g. Catalyst Solution (20% by Weight of Conc. H_2SO_4 in Glacial Acetic Acid)

Expt. no.	Reaction time, hr.	Yield, g.	Anisalacetophenone, mole-%	Sensitivity value
9	24	9.2	9.6	180
10	48	9.7	16.9	450
11	75	10.2	22.2	1600
12	100	10.5	26.5	2500
13	147	11.3	37.9	—
14	195	—	42.0	—

two sets of analyses, and the arithmetic mean of these values was used to calculate the mole per cent of polymerized vinylanisalacetophenone content of the polymer.

The light-sensitivity values included in the following tables were obtained as described elsewhere.² The values are used here simply for purposes of comparison between the various compositions.

Tables I-IV show the results obtained.

TABLE III

The Condensation of Poly(4-vinylacetophenone) with Anisaldehyde

73 g. Poly(4-vinylacetophenone) (0.5 mole); 272 g. Anisaldehyde (4 mole equivalents); 864 g. Dioxane; 73 g. Catalyst Solution (10% by Weight of Conc. H_2SO_4 in Glacial Acetic Acid)

Expt. no.	Reaction time, hr.	Yield, g.	Anisalacetophenone, mole-%	Sensitivity value
15	24	9.4	8.6	220
16	50.5	10.2	19.2	700
17	72	10.6	25.2	1,100
18	103	10.8	30.5	1,800
19	168	11.5	42.2	3,200
20	221	12.5	49.0	10,000
21	272	13.0	55.8	—

TABLE IV

The Condensation of Poly(4-vinylacetophenone) with Anisaldehyde

73 g. Poly(4-vinylacetophenone) (0.5 mole); 408 g. Anisaldehyde (6 mole equivalents); 592 g. Dioxane; 73 g. Catalyst Solution (10% by Weight of Conc. H_2SO_4 in Glacial Acetic Acid)

Expt. no.	Reaction time, hr.	Yield, g.	Anisalacetophenone, mole-%	Sensitivity value
22	24	11.0	26.6	1000
23	48	11.7	46.0	3000
24	73	12.8	52.4	3500
25	96	13.3	57.6	3500
26	170	14.5	72.0	>5000

(b) Reaction between Poly(4-vinylacetophenone) and Substituted Benzaldehydes and Other Aldehydes

A series of condensations was run in glacial acetic acid, with various aromatic aldehydes in the presence of mineral acid catalyst. The degree of conversion was not high in this series. A number of them were at a similar level, however, enabling some comparisons to be made between the products obtained.

The general method used was to add approximately 3.5 mole-equivalents of the aldehyde to a 5% solution by weight of poly(4-vinylacetophenone) in glacial acetic acid. About 0.15 mole-equivalent of concentrated sulfuric acid was added to the solution as a 10% (by weight) solution in glacial acetic acid. The solution was allowed to stand at room temperature for varying periods of time; the polymer was then isolated by pouring the solution into agitated methanol and purified as already described.

The reaction times indicated in Table V are probably close to maximum for the given conditions. Longer reaction times would probably have resulted in gelled solutions owing to crosslinkage.

As indicated earlier in the paper, relatively high degrees of substitution could be obtained in the case of benzaldehyde when it was used as a solvent, this reagent then being in large excess. This procedure

TABLE V
The Condensation of Various Araldehydes with Poly(4-vinylacetophenone)

Sample no.	Aldehyde used	Reaction time, hr.	Substitution, mole-%	Sensitivity value
27	Anisaldehyde	24	21.6	2200
28	<i>o</i> -Chlorobenzaldehyde	21	24.3	400
29	<i>p</i> -Hydroxybenzaldehyde	5.5	ca. 12-15	1000
30	3,4-Dimethoxybenzaldehyde	5.5	14.3	2500
31	<i>p</i> -Nitrobenzaldehyde	6	low	very low
32	3,4-Dichlorobenzaldehyde	24	32.4	1600*
33	Vanillin	96	10	2000-3000*
34	<i>p</i> -Dimethylaminobenzaldehyde	168	16	160 ^b
35	<i>p</i> -Dimethylaminobenzaldehyde	2	17	3200 ^c
36	<i>p</i> -Acetaminobenzaldehyde	20	10	140
37	Cinnamaldehyde	3	2.5	320
38	Anisaldehyde	5	5.8	1600
39	Anisaldehyde	8	6.6	2800
40	α - <i>n</i> -Amylcinnamaldehyde	7	—	8

* Dioxane was used instead of glacial acetic acid.

^b Sodium acetate was not used to neutralize the acid catalyst.

^c A 1:1 mixture of 2-methoxyethanol and dioxane was used instead of glacial acetic acid. Triton B catalyst was used instead of sulfuric acid.

was not generally successful with other aldehydes, for the reaction mixture frequently formed a gel and the polymeric product was insoluble. With the use of *p*-isopropylbenzaldehyde in the same manner that benzaldehyde was employed in making poly(4-vinylbenzalacetophenone), i.e., both as reagent and as solvent, a product was obtained after 18 hr. reaction time which consisted of an estimated 50 mole-% of *p*-isopropylbenzalacetophenone units. This polymer had a sensitivity value of about 280.

Using anisaldehyde both as reagent and as solvent did not furnish a soluble product of a high degree of reaction, insolubilization of the reaction mixture occurring gradually when about half of the acetophenone units had undergone reaction. However, if an equimolar mixture of benzaldehyde and anisaldehyde was used as the reagent, a polymeric product was obtained which had a high degree of reaction and high light-sensitivity. This polymer was made by the following procedure.

To a solution of 10 g. of poly(4-vinylacetophenone) dissolved in a mixture of 78 g. of benzaldehyde and 112 g. of anisaldehyde was added 10 g. of a 10% solution (by weight) of concentrated sulfuric acid in benzaldehyde. The two aldehydes were present in approximately equimolar proportions in the solution. This was allowed to stand in the dark at room temperature for 73 hr., then poured into a large volume of agitated methanol. The golden-yellow precipitate was leached in fresh methanol, then redissolved in methyl ethyl ketone containing some benzaldehyde (it was not soluble in methyl ethyl ketone alone) and reprecipitated by pouring into methanol. After another reprecipitation, the precipitate was washed in several changes of methanol and dried in the dark at room temperature. A methoxyl analysis indicated that the polymer had a poly(vinylanisalacetophenone) content of 56% by weight. The light-sensitivity was very high, having a value of 13,000.

(c) Reaction between Poly(4-vinylacetophenone) and Water-Soluble Substituted Benzaldehydes

Benzaldehyde derivatives having ionizable carboxyl and sulfonic acid substituents (as sodium salts) could not be used satisfactorily as reactants with poly(4-vinylacetophenone) in a nonaqueous organic solvent system because of their limited solubility. The presence of water inhibited the catalytic effect of sulfuric acid. The reaction could, however, be effected in solution in organic solvents containing some water if an alkaline catalyst was used. Since poly(4-vinylacetophenone) is very hy-

drophobic, the initial reaction solvent must contain a low concentration of water, but sufficient to dissolve a certain amount of the water-soluble benzaldehyde derivative. As the reaction proceeded under alkaline catalysis, water was added cautiously in sufficient amounts to keep the polymeric product in solution and to dissolve further quantities of the aldehyde. In this manner, fairly high degrees of reaction could be achieved.

(1) Reaction with Sodium *o*-Sulfobenzaldehyde.

To a solution of 65 g. of sodium *o*-sulfobenzaldehyde and 25 g. of poly(4-vinylacetophenone) in a mixture of 250 ml. of 2-methoxyethanol and 50 ml. of dioxane was added 10 g. of Triton B (a 40% aqueous solution of trimethylbenzylammonium hydroxide). The solution was still alkaline after standing for 3 days at room temperature. It was acidified by the addition of 10 ml. of glacial acetic acid and, with stirring, 250 ml. of water was added. This solution was poured into a large volume of agitated acetone and the fibrous precipitate well washed with acetone. After being washed with ethanol and extracted three times with boiling ethanol (to remove unreacted aldehyde), the polymer was dried at 40°. It was soluble in water containing either 10 wt.-% of acetone or 20 wt.-% of ethanol. Elemental sulfur analysis indicated a 61.6 mole-% reaction. The polymer had a light-sensitivity value of about 280.

(2) Reaction with 4-Methoxy-3-sodium Sulfo-benzaldehyde. Ten grams of poly(4-vinylacetophenone) was dissolved in a mixture of 100 ml. of 2-methoxyethanol and 100 ml. of dioxane. The following reagents were added to the constantly stirred solution at 10-min. intervals.

Time, min.	4-Methoxy-3-sodium sulfobenzaldehyde, g.	Triton B, g.
0	5.0	1.0
10	5.0	1.0
20	5.0	1.0
30	5.0	2.0
40	5.0	2.0
50	5.0	3.0

After the last addition, the mixture was stirred for 0.5 hr. Water was then added, dropwise, to this mixture, 50 ml. being added over the space of 40 min. After the solution had been stirred another 15 min., a further 50 ml. of water was added over a period of 15 min. This solution was allowed to stand overnight at room temperature. After 20 hr., the solution was filtered to remove a little undis-

solved aldehyde and the filtrate was acidified with acetic acid. The yellow solution was poured into a large volume of agitated acetone; the bright-yellow, fibrous precipitate was leached in three changes of fresh acetone and dried in a vacuum. This precipitate was soluble in water containing 20 wt.-% of acetone.

An analytical sample, thoroughly extracted with alcohol, had a sulfur content of 6.4%, representing a vinyl-4-methoxy-3-sodium sulfobenzalacetophenone content of 52.1 mole-%. This polymer was estimated to have a light-sensitivity value of 1400.

(3) Reaction with *p*-Carboxymethoxybenzaldehyde. *p*-Carboxymethoxybenzaldehyde was prepared by essentially the procedure described by Elkan.³

The condensation with poly(4-vinylacetophenone) was carried out in the following manner. Fifty grams of poly(4-vinylacetophenone) was dissolved in a mixture of 500 ml. of dioxane and 500 ml. of 2-methoxyethanol, and to this mixture was added 100 g. of the finely divided sodium salt of *p*-carboxymethoxybenzaldehyde prepared as just described. With continual stirring, 60 ml. of a 40% solution of benzyltrimethylammonium hydroxide was added, dropwise, over a period of about 1 hr. A 250-ml. portion of water was now added, dropwise, over a period of 0.5 hr., followed by the dropwise addition of 20 ml. of 1*N* sodium hydroxide. The solution was allowed to stand for 1.5 hr., whereupon another 250 ml. of water was added, dropwise, over a period of 25 min. After standing a further 2 hr., a third 250-ml. portion of water was added in a similar manner over a period of 15 min.

After standing overnight at room temperature, the solution was poured into a larger volume of dilute hydrochloric acid. The fine, yellow precipitate was repeatedly washed with distilled water, and the product dried in a vacuum over concentrated sulfuric acid at room temperature. The yield of polymer was 80 g. It was soluble in 2-methoxyethanol. As the sodium or triethanolamine salt, it was soluble in a 20% solution (by weight) of alcohol in water. The carboxyl content was 11.1%, indicating a molar substitution of about 60%.

DISCUSSION

It is evident from the data presented here that a general reaction between poly(4-vinylacetophenone) and aromatic aldehydes to give the corresponding arylacetophenone, or chalcone, is not clean-cut but is beset with secondary reactions

which result in netted polymeric structures. In the case of the reaction with benzaldehyde, these cross-linking reactions can be suppressed sufficiently to give soluble vinylbenzalacetophenone-containing polymers in high yield. This degree of success was not attained in the case of the substituted benzaldehydes.

The reaction between poly(4-vinylacetophenone) and anisaldehyde, when catalyzed by acids, has an equilibrium which is not generally conducive to giving high yields of the anisalacetophenone polymer. As in the case of benzaldehyde, large excesses of this aldehyde must be present in the reaction mixture to force this equilibrium in a favorable direction. Increasing catalyst concentration in the reaction mixture has a similar effect. These conditions apparently also promote the secondary cross-linking reactions, the nature of which are not known. It is known, however, that a pure poly(4-vinylbenzalacetophenone) in the isolated state in the presence of the acid catalyst will become insoluble even when benzaldehyde is not present.¹ The polymer in solution is considerably more stable in the presence of this catalyst, the time in which insolubilization takes place depending upon the concentration. The higher the dilution, the lower is the tendency to become crosslinked. Thus, the successful, useful preparation of these styryl ketone polymers is a compromise between concentration of reactants, diluent used, catalyst used and its concentration, time and temperature of reaction, as well as the aldehyde used. In this investigation no attempt was made to study the effect of all these parameters in detail, but rather to recognize those which have an effect.

It has been shown in the case of the reaction product of poly(4-vinylacetophenone) and benzaldehyde that the light-sensitivity values of the products were affected by the degree of reaction and the molecular weight of the polymer (as indicated by viscosity data). Thus, the polymers shown in Table V are comparable only at approximately equivalent reaction levels. Although the same parent poly(4-vinylacetophenone) was used in the preparation of these polymers, the final molecular weights could be quite different. This could be due to some intermolecular reaction of reactive double bonds to give products of enhanced molecular weight. Any comparison of the light-sensitivity values given must therefore be very general. It is evident, however, that those polymers prepared by using *p*-methoxy-, *p*-hydroxy-, and *p*-dialkylaminobenzaldehyde with poly(4-vinyl-

acetophenone) show a generally higher sensitivity to light at an approximately equivalent degree of reaction. These electron-donating substituents generally impart a hypsochromic shift in the absorption of the corresponding chalcone.⁴ This is true in both the hydrophobic and hydrophilic products obtained. While few examples of the use of benzaldehydes having electron-withdrawing substituents are available in this work (a number of such aldehydes gave products of poor solubility and hence questionable sensitivity data), those available tended towards lower sensitivities as compared with condensation products obtained from unsubstituted benzaldehyde. Thus, *p*-dimethylaminobenzaldehyde under alkaline catalysis gave a polymeric product where the amino nitrogen was not in the salt form. This polymer was about 20 times more sensitive than a polymer of about equivalent degree of reaction using sulfuric acid catalyst and isolated largely as the sulfate. This is to be expected if one takes into account the light-absorption characteristics of such condensation products.⁵

In many of the instances just discussed, only moderate degrees of reaction were achieved. Even the use of virtually complete darkness during the synthesis of these polymers did not eliminate solubility difficulties.

In one instance where a mixture of benzaldehyde and anisaldehyde was used both as solvent and as reagent, a product was obtained having good solubility and very high sensitivity. The vinyl(anisalacetophenone) content of the polymer was about 56 mole-%, the remainder probably consisting of vinyl(benzalacetophenone) units.

It is clear that a substituent on a carbon atom adjacent to the styryl ketone double bond severely lowers the light-sensitivity, presumably owing to steric factors. On the other hand, the vinyllog of the styryl ketone group, such as that obtained by using cinnamaldehyde, possesses a very high sensitivity to light even at low order of reaction. Such polymers, however, have poor stability, some of the samples becoming insoluble in a few days or weeks. Many of the other styryl ketone polymers, if free from acid or alkaline contaminants, retain good solubility even after years of storage, if they are not exposed to light or elevated temperatures.

References

1. Unruh, C. C., *J. Appl. Polymer Sci.*, **2**, 358 (1959).
2. Minsk, L. M., J. G. Smith, W. P. Van Deusen, and J. F. Wright, *J. Appl. Polymer Sci.*, **2**, 302 (1959).

3. Elkan, T., *Ber.*, **19**, 3041 (1886).
4. Szmant, H. H., and A. J. Basso, *J. Am. Chem. Soc.*, **74**, 4397 (1952).
5. Phillips, A. P., *J. Org. Chem.*, **17**, 333 (1947).

Synopsis

The preparation of condensation products of poly(4-vinylacetophenone) with various substituted benzaldehydes is described. As in the case of the products obtained by condensing the poly(4-vinylacetophenone) with benzaldehyde, these, too, show to varying degrees the property of becoming insoluble when exposed to light. This sensitivity to light is generally higher where the aldehyde used contains electron-donating substituent groups in the *para*-position. This, in turn, is also related to the ability of such products to absorb a larger proportion of the longer wavelength portion of the emitted light.

Résumé

La préparation de produits de condensation de la poly-4-vinylacétophénone avec divers benzaldéhydes substitués a été décrite. Dans le cas des produits obtenus par condensation de la poly (4-vinyl-acétophénone) avec le benzaldéhyde

on constate, à des degrés divers, une insolubilisation lors de l'exposition à la lumière. Cette sensibilité à la lumière est généralement plus accentuée lorsque l'aldéhyde utilisé est substitué en position *para* par des groupes électrodonneurs. Ceci est d'autre part relié à l'aptitude qu'ont de tels produits à absorber une part plus importante des variations de longueurs d'onde élevées de la lumière émise.

Zusammenfassung

Die Darstellung von Kondensationsprodukten aus Poly(-4-vinylacetophenon) und verschiedenen, substituierten Benzaldehyden wird beschrieben. So wie im Falle der durch Kondensation von Poly-(4-vinylacetophenon) mit Benzaldehyd erhaltenen Produkte, zeigen auch diese in verschiedenem Masse die Eigenschaft, bei Einwirkung von Licht unlöslich zu werden. Diese Lichtempfindlichkeit ist bei Verwendung von Aldehyden mit elektronenliefernden substituierenden Gruppen in *para*-Stellung im allgemeinen höher. Daher steht die Empfindlichkeit auch wieder in Beziehung zu der Fähigkeit solcher Produkte, einen grösseren Anteil des längerwelligen Bereiches des emittierten Lichtes zu absorbieren.

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